

## Effect of Cr concentration on resistance switching in Cr-doped SrZrO<sub>3</sub> films and surface accumulation of Cr ions

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The role of Cr ions in the resistance switching (RS) of Cr-doped SrZrO<sub>3</sub> films has been investigated by x-ray photoelectron spectroscopy and electric current measurements. The results show that the RS behavior depends on the Cr concentration, substrate temperature during film growth, and oxygen pressure during the postannealing process. Migration of Cr<sup>3+</sup> ions to the surface makes the surface Cr rich, and thus, appreciable RS is observed. These observations suggest that the RS behavior can be controlled by trapping and releasing Cr carriers in the interface region between the film and the electrode. © 2010 American Institute of Physics. [doi:10.1063/1.3499626]

Recently, Cr-doped perovskite (Cr:SrZrO<sub>3</sub>, Cr:SrTiO<sub>3</sub>) systems have been actively investigated because they show promising behaviors as a resistive random access memory material with several advantages such as low operational power, capability of high-density integration, and high-speed write-erase operations.<sup>1-3</sup> However, despite numerous phenomenological studies on resistance switching (RS), the origin of RS in Cr:SrZrO<sub>3</sub> films is not fully understood yet. Some researchers have claimed that RS exists in a perovskite oxide without doping,<sup>4</sup> while other groups have reported that it was not reproducible.<sup>5</sup> Meijer *et al.*<sup>6</sup> suggested that RS originates from an electron trapping/detrapping process through valence changes in Cr ions in a Cr:SrTiO<sub>3</sub> single crystal. On the other hand, Janousch and co-workers<sup>7,8</sup> subsequently reported that rather than valence changes in Cr ions, an oxygen-vacancy drift could be the main reason for RS. Furthermore, some other groups reported that RS may be originating from the mixed valence states of cations such as Cr, Ce, and Mn.<sup>9-11</sup>

In this study, we investigated the role of Cr ions in the RS behavior of Cr-doped SrZrO<sub>3</sub> films by using x-ray photoelectron spectroscopy (XPS) and electrical current measurements. We determined the factors controlling RS behavior in Cr:SrZrO<sub>3</sub> films by measuring the electrical properties of samples grown from targets with various Cr concentrations (0, 0.1, 0.2, and 0.3 mol % in the target), grown at different substrate temperatures (T=400, 550, and 700 °C), and postannealed under various oxygen partial pressures (P<sub>O<sub>2</sub></sub>=5.0×10<sup>-6</sup>, 2.0×10<sup>-1</sup>, and 3.3×10<sup>2</sup> Torr). We found that the electrical properties of these films were different; the best RS behavior was observed in a Cr:SrZrO<sub>3</sub> film with a Cr concentration of 0.2 mol %, which was grown at the substrate temperature T=700 °C and postannealed under P<sub>O<sub>2</sub></sub>=5.0×10<sup>-6</sup> Torr. *In situ* XPS measurements on this film showed that Cr ions migrated onto the surface and that the valence of Cr ions is 3+. This implies that the Cr ions at the interface region between the Cr:SrZrO<sub>3</sub> film and electrode

play important roles in the RS behavior of Cr:SrZrO<sub>3</sub> films.

Cr:SrZrO<sub>3</sub> films (100–200 nm thick) were grown in a preparation chamber (~10<sup>-8</sup> Torr) on SrRuO<sub>3</sub> (20 nm thick)/SrTiO<sub>3</sub>(100) substrates by employing pulsed laser deposition using a neodymium-doped yttrium aluminium garnet (Nd:YAG) laser (λ=266 nm) and Cr:SrZrO<sub>3</sub> targets. The energy and repetition rates of the laser pulses were 0.75 J/cm<sup>2</sup> and 10 Hz, respectively. The films were transferred *in situ* to a main chamber equipped with a VG CLAM4 spectrometer for XPS measurements. The base pressure of the main chamber was 1×10<sup>-10</sup> Torr. The structures of the deposited films were subsequently verified by x-ray diffraction measurements in air; the films were found to grow epitaxially along the (100) direction at high substrate temperatures (T=550 and 700 °C), while they become polycrystalline at low temperatures (T=400 °C). For the I-V measurements, a metal electrode (Pt or Au) was deposited on the Cr:SrZrO<sub>3</sub> films by the sputtering method. The current was measured at room temperature at the probe station with a current meter (HP4155A).

Figure 1 shows the I-V characteristics of Cr:SrZrO<sub>3</sub> films that have different Cr concentrations in the targets (0, 0.1, 0.2, and 0.3 mol %). The films were grown at 700 °C under P<sub>O<sub>2</sub></sub>=2.0×10<sup>-1</sup> Torr and postannealed at 400 °C under P<sub>O<sub>2</sub></sub>=5.0×10<sup>-6</sup> Torr. The SrRuO<sub>3</sub> layer was used as a bottom electrode and grounded during I-V measurements. A voltage was applied across electrodes until the threshold voltage was generated, which process is usually called “forming.” In general, the threshold voltages of Cr:SrZrO<sub>3</sub> films were sensitive to the film thickness and quality. In undoped SrZrO<sub>3</sub> films, no leakage current (<1 pA) was observed. The leakage current gradually increased with the Cr concentration and is proportional to the Cr concentration in the low resistance state (LRS). This suggests that the Cr ions in the films supply charge carriers to form the LRS. In particular, the SrZrO<sub>3</sub> films doped with 0.1 and 0.2 mol % Cr show RS hysteresis between the LRS and high resistance state (HRS) but the film doped with 0.3 mol % Cr only shows an Ohmic dependence without RS hysteresis. The re-

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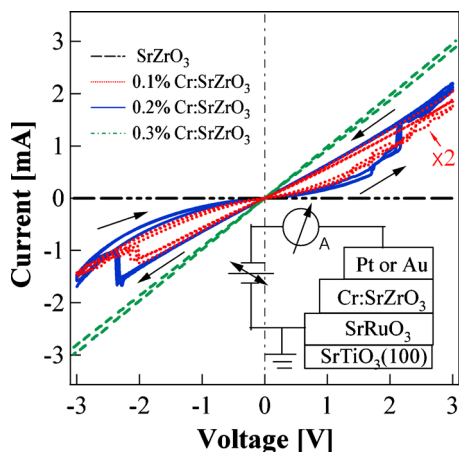


FIG. 1. (Color online) I-V curves of the Cr: SrZrO<sub>3</sub> films (Cr: 0, 0.1, 0.2, and 0.3 mol %). Schematic diagram shows the sample structure used for applying an electric field across the film. All the films were grown at a substrate temperature of 700 °C ( $P_{O_2}=2.0 \times 10^{-1}$  Torr) and postannealed at 400 °C ( $P_{O_2}=5.0 \times 10^{-6}$  Torr).

sistance of this 0.3 mol % film can be considered as LRS judging from its magnitude, and the absence of HRS in this film probably indicates that large Cr concentrations give rise to too many charge carriers to sustain HRS. The fact that Cr ions provide charge carriers in this system is also supported by previous reports that the ratio of resistance change increases with the dopant concentration.<sup>12,13</sup>

It is well known in surface science that some atomic species may migrate to the surface during film growth. To verify this possibility in our case, we have compared the core-level peak intensities in the XPS spectra for films grown at different substrate temperatures. The spectra will give the stoichiometry near the surface region since the probing depth of XPS measurements is limited to only a few atomic layers from the surface. Figure 2 shows the (a) O 1s, (b) Zr 3d, (c) Sr 3d, and (d) Cr 2p XPS spectra of the 0.2 mol % Cr: SrZrO<sub>3</sub> films that were deposited at three different growth temperatures of 400, 550, and 700 °C under  $P_{O_2}$  of  $2.0 \times 10^{-1}$  Torr. The films were subsequently annealed for 30 min at 400 °C under  $P_{O_2}$  of  $5.0 \times 10^{-6}$  Torr. The binding energy (BE) was calibrated by setting the C 1s BE of the adsorbed hydrocarbon as 285.0 eV. The features at the higher BE in O 1s and Sr 3d spectra of the film grown at 400 °C [Figs. 2(a) and 2(c)] indicate that phases such as SrO<sub>x</sub> were formed because of the low substrate temperature. Those phases gradually disappeared as the growth temperature increased. Moreover, a substantial increase in the Cr 2p peak intensities was observed in Fig. 2(d) at high-temperature growth. The peaks of the Cr 2p<sub>3/2</sub> (2p<sub>1/2</sub>) core level were clearly observed at 576.8 (586.6) eV when the growth temperature was 700 °C, whereas both peaks were not detected in the other films grown at  $T < 600$  °C. The high temperature helps the mobile Cr ions to diffuse into the surface region during the deposition. As shown in Figs. 2(a)–2(c), BEs of O 1s, Zr 3d, and Sr 3d related to the SrZrO<sub>3</sub> phase increase uniformly by 0.2 eV as the growth temperature is increased from 400 to 550 °C, which probably means that the Fermi energy ( $E_F$ ) is shifted toward the conduction band minimum by 0.2 eV because of oxygen vacancy creation. On

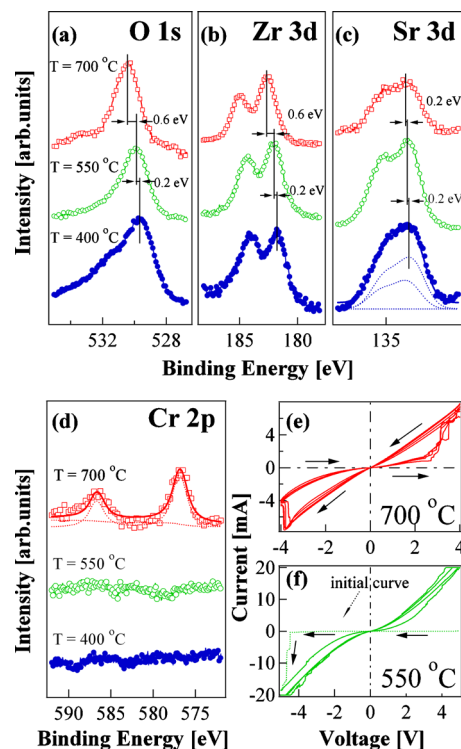


FIG. 2. (Color online) XPS spectra of (a) O 1s, (b) Zr 3d, (c) Sr 3d, and (d) Cr 2p core levels in Cr: SrZrO<sub>3</sub> (Cr: 0.2 mol %) films taken before the deposition of the top electrode and forming. The samples were grown at 400, 550, and 700 °C with  $P_{O_2}=2.0 \times 10^{-1}$  Torr and postannealed at 400 °C with  $P_{O_2}=5.0 \times 10^{-6}$  Torr. The I-V characteristics of the samples at growth temperatures of 700 °C and 550 °C are appended in (e) and (f), respectively.

the other hand, the film grown at 700 °C has higher BEs of O 1s and Zr 3d than the film grown at 550 °C by 0.6 eV, whereas BE of Sr 3d is shifted by only 0.2 eV. This suggests that Zr, O, and migrated Cr ions participate in the change in surface chemistry, which leads to the chemical shift in the spectra of Zr 3d and O 1s. We also estimated the Cr concentration at the film surface by using the XPS peak intensity and the empirical atomic sensitivity factor of the Cr 2p core level. The [Cr]/[Sr] concentration ratios of the films were considerably higher than the nominal values of the targets: ~4%, ~6%, and ~9% for 0.1 mol %, 0.2 mol %, and 0.3 mol %-Cr-doped SrZrO<sub>3</sub> targets, respectively.

Figures 2(e) and 2(f) show the I-V curves of Cr: SrZrO<sub>3</sub> films grown at 550 °C and 700 °C, respectively. The film grown at 550 °C has a huge initial resistance and its RS was not observed even after the forming process with high voltage. In contrast, the I-V curve of the film grown at 700 °C clearly shows RS behavior with two resistance states, LRS and HRS. We believe the main cause of this change in I-V characteristics is the migrated Cr ions. We could conceive other factors such as the difference of crystal structure or the amount of oxygen vacancies as the possible cause. However, both films grown at 550 and 700 °C were epitaxial overall. And judging from the core-level shifts shown in Figs. 2(a)–2(c), there occurred chemical changes with the migration of Cr ions as the growth temperature was increased from 550 to 700 °C. The change in oxygen vacancies between these two growth temperatures is probably similar to the case

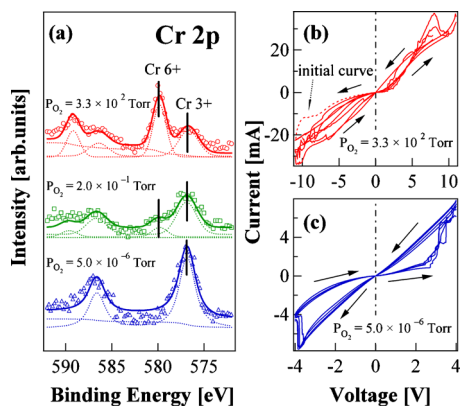


FIG. 3. (Color online) (a) XPS spectra of Cr: SrZrO<sub>3</sub> (Cr: 0.2 mol %) films taken before the deposition of the top electrode and forming. The data were taken with  $\theta=50^\circ$ , where  $\theta$  is the angle between the sample and the electron energy analyzer [see Fig. 4(b) below]. The samples were grown at the substrate temperature 700 °C ( $P_{O_2}=2.0 \times 10^{-1}$  Torr) and postannealed at 400 °C ( $P_{O_2}=3.3 \times 10^2$  Torr,  $2.0 \times 10^{-1}$  Torr, and  $5.0 \times 10^{-6}$  Torr). The I-V characteristics of the samples in the case of  $P_{O_2}=3.3 \times 10^2$  Torr and  $5.0 \times 10^{-6}$  Torr are appended in (b) and (c), respectively. (c) reproduces the same curve with Fig. 2(e).

of 400 and 550 °C, judging from the BE shift (0.2 eV) of Sr 3d peak. Although the RS mechanism may also be closely related to oxygen vacancies as reported on the study of undoped SrTiO<sub>3</sub> single crystal,<sup>4</sup> it should be noted that the amount of Cr ions (roughly  $10^{21}$  cm<sup>-3</sup>) at the surface of our samples was even larger than the amount of oxygen vacancies which lead to metal-insulator transition in SrTiO<sub>3</sub> single crystal (roughly  $10^{14}$ – $10^{20}$  cm<sup>-3</sup>).

We further investigated the valence of Cr ions using the XPS technique. Cr is mostly believed to substitute Zr(Ti)<sup>4+</sup> ions in SrZr(Ti)O<sub>3</sub>,<sup>14</sup> but various (mixed) valence states of Cr ions could be realized with accompanying oxygen vacancies and lattice distortion. The Cr: SrZrO<sub>3</sub> films deposited under  $P_{O_2}=2.0 \times 10^{-1}$  Torr at 700 °C were postannealed for 30 min at 400 °C under different  $P_{O_2}$  values. Figure 3(a) shows the Cr 2p XPS spectra of the samples annealed under  $P_{O_2}=5.0 \times 10^{-6}$  Torr,  $2.0 \times 10^{-1}$  Torr, and  $3.3 \times 10^2$  Torr. When the film was annealed under  $P_{O_2}=5.0 \times 10^{-6}$  Torr, the XPS spectrum showed a doublet near the BEs of 576.8 and 586.6 eV corresponding to the Cr ion valence of +3.<sup>15</sup> When  $P_{O_2}$  of the postannealing process was increased, two peaks near the BEs of 579.8 and 589.3 eV grew significantly. This indicates the formation of Cr<sup>6+</sup> states since the BE of the Cr 2p core level increases by 2.8–3.2 eV for the valence change from 3+ to 6+.<sup>15</sup> The concentration ratio of Cr<sup>6+</sup>/Cr<sup>3+</sup> increased with the amount of oxygen gas in the postannealing chamber. The surface chemistry strongly influences the electrical properties of the film samples. The I-V curve of the sample annealed under  $P_{O_2}=3.3 \times 10^2$  Torr is shown in Fig. 3(b). Although the I-V curves of the low  $P_{O_2}$  ( $=5.0 \times 10^{-6}$  Torr) sample exhibit well-defined RS and threshold voltage [Fig. 3(c)], those of the high  $P_{O_2}$  ( $=3.3 \times 10^2$  Torr) sample exhibit ill-formed non-Ohmic characteristics [Fig. 3(b)]. Therefore, we speculate that Cr<sup>3+</sup> ions, and not Cr<sup>6+</sup> ions, at the surface improve the RS behaviors of the Cr: SrZrO<sub>3</sub> films.

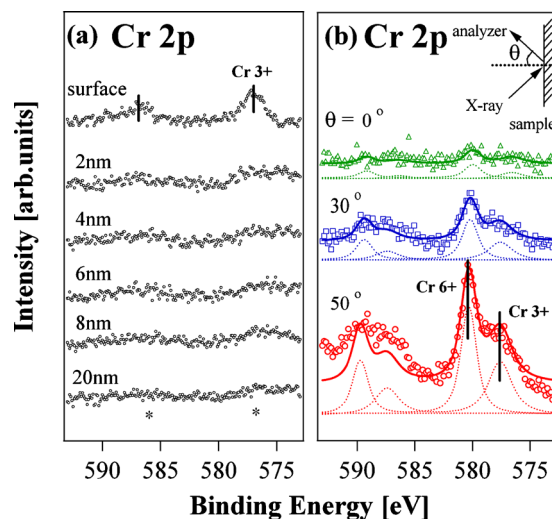


FIG. 4. (Color online) (a) Depth-profile XPS of Cr: SrZrO<sub>3</sub> (Cr: 0.3 mol %) film, which was grown at the substrate temperature 700 °C ( $P_{O_2}=2.0 \times 10^{-1}$  Torr) and postannealed at 400 °C ( $P_{O_2}=5.0 \times 10^{-6}$  Torr). The broad humps denoted as asterisks originate from the O 1s plasmon sidebands so they are not relevant to the Cr concentration. (b) The angle-dependent XPS of Cr: SrZrO<sub>3</sub> (Cr: 0.2 mol %) film, which was grown at the substrate temperature 700 °C ( $P_{O_2}=2.0 \times 10^{-1}$  Torr) and postannealed at 400 °C ( $P_{O_2}=3.3 \times 10^2$  Torr) and their fitting lines. The probing depth increases effectively with increasing angle  $\theta$  between the sample normal and the detector.

To determine the distribution of Cr ions on the surface region, we performed depth-profile XPS with successive Ar<sup>+</sup>-sputtering. The 0.3 mol % Cr: SrZrO<sub>3</sub> film grown at 700 °C and annealed under  $P_{O_2}=5.0 \times 10^{-6}$  Torr was etched by 2 nm step down to 20 nm. Figure 4(a) shows that the peaks at BEs of 576.8 and 586.6 eV, which correspond to Cr<sup>3+</sup>, disappeared when the film was etched by 2 nm. This indicates that most of the Cr ions exist within a 2 nm range from the surface. This fact is also confirmed by the angle-dependent XPS shown in Fig. 4(b), which displays three Cr 2p spectra of 0.2 mol % Cr: SrZrO<sub>3</sub> film taken with three different detection geometries, i.e., the angle  $\theta$  between the sample normal and the electron energy analyzer. The surface sensitivity of XPS increases drastically with increasing  $\theta$  because of the limited electron mean free path. The Cr 2p peaks from both Cr<sup>3+</sup> and Cr<sup>6+</sup> are clearly seen at a large angle ( $\theta=50^\circ$ ), while those are barely observable at the sample normal direction ( $\theta=0^\circ$ ). This confirms that a substantial amount of Cr ions exists only at the film surface to form the Cr rich surface.

The increasing of the ratio of Cr<sup>6+</sup>/Cr<sup>3+</sup> might indicate the emergence of segregated phases such as CrO<sub>3</sub> or SrCrO<sub>4</sub>.<sup>16</sup> These unstable phases are known to be easily removed by thermal treatments in vacuum. However, annealing under high oxygen pressure allows the existence of an oxygen-rich phase, such that the Cr ions lose more electrons to the oxygen atoms near the surface. Subsequent strong electric fields might release the electrons and create too many electrical leakage paths to sustain the HRS, which may be the reason for the absence of RS behavior in this film. On

the other hand, Cr<sup>3+</sup> ions seem to play an important role for the emergence of RS. If Cr<sup>3+</sup> ions form a charge reservoir and act as charge traps in insulating SrZrO<sub>3</sub> films, an appreciable RS can be caused by the storage (HRS) and release (LRS) of charges through changing Cr valences underneath the top electrode. The charge transfer process caused by valence change in Cr ions has been reported elsewhere.<sup>17,18</sup> In our Cr-doped SrZrO<sub>3</sub> films, most of Cr<sup>3+</sup> ions were distributed underneath the top electrode. Therefore this can help the process of trapping and releasing charges more efficiently in response to the electric field.

In conclusion, it has been experimentally shown that the RS behavior of Cr:SrZrO<sub>3</sub> depends strongly on the chemistry of the Cr-rich domain near the top electrode. The optimum RS behavior was observed in the films that were grown at high substrate temperature (~700 °C) which induces Cr migration to the surface region and postannealed at low oxygen partial pressures ( $P_{O_2} < 10^{-5}$  Torr) which maintains the valence of Cr ions as 3+. The abundance of the stable Cr<sup>3+</sup> appears to be prerequisite for appreciable RS behavior in Cr-doped SrZrO<sub>3</sub>.

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